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FREEZING CURVES OF THE SYSTEMS BENZENE-ETHER AND BENZENE-ACETONE.

By Shiro YAMAMURA.

Received July 12, 1923. Published September 28, 1926.

The System Benzene-Ether. The melting points of the mixtures of benzene and ethyl ether was studied by Pickering.[1] But his results is not complete one and want the part of 80–100 percent ether.

My apparatus for the measurement of the freezing point of the mixture was very similar to that usually used in the determination of the freezing point depression of dilute solutions. Special precautions, however, were taken to prevent the introduction of water vapour into the liquid mixture. 10–15 c.c. of liquid mixture was introduced into a glass tube in which a pentane thermometer and a stirrer were inserted. The tube was cooled from outside with cooling agent such as solid carbon dioxide or liquid air. To regulate the rate of cooling of the liquid, the tube was protected with a partially evacuated Dewar vessel which then dipped into the cooling agent. A pentane thermometer having the certificate of the "Physikalisch-Technische Reichsanstalt" was used for the measurement of low temperature. This kind of thermometer, however, cannot be used to measure the temperature in greater accuracy than half a degree. Moreover the correction of reading for the exposed thread of pentane amounted to a few degrees in some cases, so this must be taken into consideration in the determination of freezing point.

The results of the measurement were as follows.

Mol % of ether.	Freezing point.	Mol % of ether.	Freezing point.
	°		°
0 (pure C_6H_6)	+ 5.1	74.5	− 61.3
5.1	+ 1.7	80.3	− 71.7
7.0	+ 0.4	82.0	− 74.5
14.9	− 4.3	82.3	− 79.
16.0	− 4.8	85.1	− 88.5
25.1	− 11.2	87.7	− 94.
30.6	− 14.9	90.4	−105.
35.1	− 18.6	91.3	−106.
39.5	− 22.6	92.4	−115.5
44.9	− 27.0	92.7	−118.5
49.6	− 33.0	94.8	−126.5
55.0	− 36.9	94.9	−126.5
59.6	− 43.4	97.1	−125.
64.1	− 48.0	97.6	−124.5
69.7	− 52.5	100. (pure $C_4H_{10}O$)	−123.5 (metastable form)

(1) Pickering, *J. Chem. Soc.*, 63 (1893), 998.

Graphically it becomes as Fig. 1.

The System Benzene-Acetone. The method of measurement is quite the same as the system mentioned above. The results were as follows.

Mol % of acetone.	Freezing point.	Mol % of acetone.	Freezing point.
0 (pure C_6H_6)	+ 5.1°	81.8	− 61.°
21.3	− 5.	84.2	− 68.
33.4	− 15.	86.0	− 72.
46.7	− 22.	89.1	− 83.
52.0	− 25.	89.9	− 87.
59.5	− 32.	96.6	− 96.0
69.1	− 40.	100. (pure C_3H_6O)	− 94.8

It is shown graphically in Fig. 2.

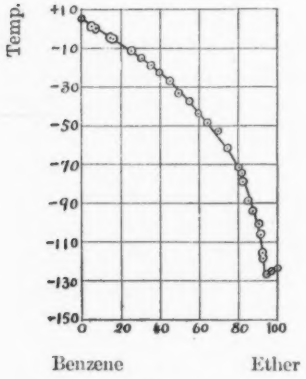

Fig. 1.

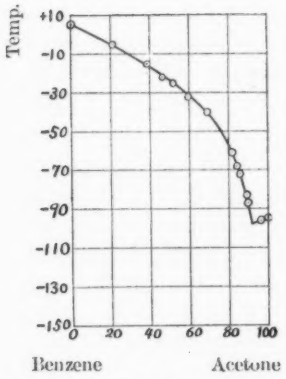

Fig. 2.

The author's thanks are due to Prof. J. Sameshima for his kind guidance.

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ON THE DERIVATION OF ADSORPTION ISOTHERMS.

By Bun-ichi TAMAMUSHI.

Received July 26, 1926. Published September 28, 1926.

With regard to a surface containing adsorbed substance Volmer[1] assumed the following characteristic equation,

$$(\gamma_0-\gamma)\left(\frac{1}{u}-\beta\right)=RT \quad \cdots\cdots(1)$$

in which γ_0 is the surface tension of pure solvent, γ that of solution, u the excess of solute in unit surface, so that according to Volmer's notation $\frac{1}{u}=\Omega$ being the area of the surface where one mol of the solute is adsorbed, β the actual area occupied by the molecules of solute per mol in the surface, R the gas constant, and T the absolute temperature.

Kar[2] has given this equation a theoretical foundation by the method of statistical mechanics and also from this equation he has derived the adsorption isotherm of Langmuir[3] which is expressed as follows :

$$C=\frac{ku}{1-\alpha Nu} \quad \cdots\cdots(2)$$

where C is the concentration of solute in the interior of solution, u the excess of solute in the surface, α the area of a molecule of solute, and N Avogadro's number. Therefore αN is equal to β in equation (1).

To derive the equation of Langmuir from that of Volmer, another equation which involves γ, C and u will be necessary. The following form fitts for the purpose :

$$\frac{u}{1-u\beta}=-\frac{C}{RT}\frac{d\gamma}{dC} \quad \cdots\cdots(3)$$

This may, namely, be called a revised equation of Gibbs since a due correction being made on the left side of the original equation.

Now differentiating equation (1) at constant temperature,

$$-d\gamma=\frac{RT}{(1-u\beta)^2}du$$

(1) *Z. physik. Chem.*, 115 (1925), 253.
It may be remarked that the equation of Volmer represent a particular case of Gibbs' equation when the solution is so dilute as we can put $C=dC$ and $\gamma_0-\gamma=-d\gamma$ in the latter equation.

(2) *Physik. Z.*, 26 (1925), 615.

(3) *J. Am. Chem. Soc.*, 40 (1918), 1361.

and from equation (3) we get

$$-d\gamma = RT\frac{u}{1-u\beta}\frac{dC}{C}.$$

Equating these relations,

$$\frac{RT}{(1-u\beta)^2} = RT\frac{u}{1-u\beta}\frac{dC}{C}.$$

Hence we have

$$\frac{dC}{C} = \frac{du}{u(1-u\beta)}.$$

By integration

$$\int\frac{dC}{C} = \int\left(\frac{1}{u}+\frac{\beta}{1-u\beta}\right)du + \text{const.}$$

so that we have

$$\ln C = \ln u - \ln(1-u\beta) + k$$

where k is a constant of integration.
Thus it becomes

$$C = \frac{ku}{1-u\beta}$$

or

$$C = \frac{ku}{1-aNu}.$$

This is the adsorption isotherm of Langmuir which was obtained in his theory of monomolecular film and also experimentally confirmed by him.

Now the Gibbs' equation in its original form will be used instead of the equation (3) and γ will be eliminated in the following manner.

$$u = -\frac{C}{RT}\frac{d\gamma}{dC} \quad \cdots\cdots(4)$$

or

$$-d\gamma = \frac{dC}{C}uRT,$$

equating this and the differential of equation (1), we have

$$\frac{dC}{C} = \frac{du}{u(1-u\beta)^2}.$$

By integration

$$\int\frac{dC}{C} = \int\frac{du}{u(1-u\beta)^2} + \text{const.}$$

i.e.

$$\int \frac{dC}{C} = \int \left(\frac{1}{u} + \frac{\beta}{1-u\beta} + \frac{\beta}{(1-u\beta)^2} \right) du + \text{const.}$$

therefore it becomes

$$\ln C = \ln u - \ln (1-u\beta) + \frac{1}{1-u\beta} + \lambda$$

in which λ is an integration constant.
Hence we obtain

$$C = \frac{u}{1-u\beta} e^{\lambda + \frac{1}{1-u\beta}}$$

or

$$C = \lambda' \frac{u}{1-u\beta} e^{\frac{u\beta}{1-u\beta}} \quad \cdots\cdots\cdots\cdots\cdots\cdots (5)$$

where λ' denotes a certain constant.

This formula is analogous to that of Schmidt[1] as will easily be shown in the following transformation.

Since we can put $u = \omega x$, x being the total amount of adsorption, and $\frac{1}{\omega}$ the area of adsorption surface, equation (5) is transformed into

$$C = \lambda' \frac{\omega}{1-\omega\beta x} x e^{\frac{\omega\beta x}{1-\omega\beta x}}.$$

or

$$C = \lambda' \omega e^{\omega\beta S} \frac{x}{1-\omega\beta x} e^{\omega\beta\left(\frac{x}{1-\omega\beta x} - S\right)}$$

Here S denotes the maximum amount of adsorption. Moreover put

$$\lambda' \omega e^{\omega\beta S} = \frac{K}{S}, \qquad \omega\beta = -A,$$

then we have

$$C = \frac{K}{S} \frac{x}{1-\omega\beta x} e^{A\left(S - \frac{x}{1-\omega\beta x}\right)}.$$

(1) *Z. physik. Chem.*, **77** (1911), 645 ; **88** (1913), 677.

Comparing this equation with that of Schmidt i.e.,

$$C=\frac{K}{S}xe^{A(S-x)}$$

we see that the former is identical with the latter provided that x being corrected by $(1-u\beta)$.

The effect of the correction term $(1-u\beta)$ in these equations in consideration may not be so great, but it affects in such sense as to make the value of u greater, since $(1-u\beta)<1$. This relation seems to afford an explanation for the deviation seen in the experimental verifications of the equation of Gibbs. In the works of this kind the calculated value of u tends mostly to be smaller than that of the observed one, as was the case in the work of Mc Lewis[1] or of Donnan and Barker.[2] The fact, however, is not simple for other possible corrections which would affect the balance of energy might also be taken into account.

Now if the equation of Volmer is simplified by dropping the correction β, we have

$$(\gamma_0-\gamma)\frac{1}{u}=RT \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(1')$$

Moreover, if a correction analogous to van't Hoff's coefficient be introduced into this equation we have

$$(\gamma_0-\gamma)\frac{1}{u}=iRT \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(1'')$$

in which i is a certain correction factor. Combining either one of these equations with equation (4) and (3) respectively so as to eliminate γ in the similar way as before, there are obtained several adsorption isotherms.

From equations (1′) and (4), $C=ku$ that is, Henry's law follows as the simplest case, and from (1′) and (3) we get $C=ue^{-\beta u+\text{const.}}$ i.e. a formula of Schmidt's type. Similarly from (1″) and (4) we obtain $C=ku^i$ i.e. a formula which is identical with that of Freundlich, and from (1″) and (3) $C=u^ie^{-i\beta u+\text{const.}}$, a formula which is of Freundlich's type and expresses also the state of saturation.

Further studies on this subject will be done.

In conclusion, the author wishes to express his cordial thanks to Prof. M. Katayama for his kind guidance.

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(1) *Phil. Mag.*, (6), **15** (1908), 499.
(2) *Proc. Roy. Soc.*, A, **85** (1911), 557.

A RELATION BETWEEN ORTHOBARIC DENSITIES.

By Jurô HORIUCHI.

Received August 9, 1926. Published September 28, 1926.

The distribution of infinitesimal molecules in phases having different potential energies is expressed in the following classical equation,

$$\frac{N_1}{N_2} = e^{\frac{-(\psi_1-\psi_2)}{RT}} \quad \text{or} \quad -(\psi_1-\psi_2) = RT\ln\frac{N_1}{N_2},$$

where N_1 and N_2 denote the molecular density in the phase of the potential energy ψ_1 and ψ_2 respectively. Now to discuss the orthobaric state of coexistent liquid and vapour, the molecule cannot be regarded as of infinitesimal size. Consequently we can introduce a proper correction to either side of the above equation. In the following discussion, it is supposed that due correction has been introduced in ψ, so that $\psi_1-\psi_2$ does not express the actual internal heat of evaporation, but the increase of potential energy when the molecule of infinitesimal size be transfered from liquid to the gaseous phase. The foregoing equation can be modified in the following form,

$$-(\psi_1-\psi_2)=\psi=RT\ln\frac{D_l}{D_g}=RT\ln\frac{V_g}{V_l}, \quad \cdots\cdots\cdots\cdots (1)$$

where V_l, D_l, V_g and D_g represent the molecular volume and the density of liquid and those of vapour respectively. Under the assumption that the internal pressure should be proportional to the square of the density, van der Waals and his followers gave an expression a/v^2 for the internal pressure. Integrating this, we obtain the following relation for the potential difference between two states having the molecular volume V_g and V_l,

$$\psi=\int_{V_l}^{V_g}\frac{a}{V^2}dV=a\left(\frac{1}{V_l}-\frac{1}{V_g}\right)=RT\ln\frac{V_g}{V_l}.$$

It is well known that this does not agree with experiments. However subtracting a certain quantity E, characteristic to individual substances, the resulting equation was found to be concordant with actual measurements i.e.

$$\psi=RT\ln\frac{V_g}{V_l}=A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right) \cdots\cdots\cdots\cdots (2)$$

where A is a constant characteristic to each substance. This expression may be regarded as a proper form to express virtual internal heat of vaporization for infinitesimal molecules. In the literatures there are found equations

analogous to (2). Goebel[1] derived a equation of state for gases, giving an expression $\frac{a}{(V-a)^2}$ for the internal pressure. The region of validity of his equation was found to be $t>t_k$, $p>p_k$, and $V>1.9b$, and it failed at the temperature and pressure below that of the critical point.

Keyes,[2] adopting the form $\frac{A}{(V+l)^2}$ for the internal pressure, has shown that the value of l is negative for hydrogen and air, while it is positive for mathane and others.

Now, the calculation of the present author ranges from the critical temperature to those below the room temperature and shows good agreement with the experimental data. Goebel's equation has the purpose to express actual internal pressure, while that of the present author intends to express a relation between orthobaric densities. Consequently these two equations, though resembling in their form, are essentially different, and the numerical values of constants being of course quite different.

If we assume that the internal heat of vaporization L_i can be obtained by integrating Goebel's expression, then we have

$$L_i=\int_{V_l}^{V_g}\frac{a}{(V-a)^2}\,dV=\frac{a}{V_l-a}-\frac{a}{V_g-a} \quad \cdots\cdots\cdots\cdots(3)$$

Combining (3) with Dieterici's empirical equation,[3] $L=CRT\ln V_g/V_l$, where C is close to 1.7, we obtain a relation

$$CRT\ln\frac{V_g}{V_l}=\frac{a}{V_l-a}-\frac{a}{V_g-a} \quad \cdots\cdots\cdots\cdots(4)$$

Thus equation (2) is formally equivalent to the Goebel's equation, extended to orthobaric states and combined with Dieterici's rule. In equation (2), however, the actual value of L_i is not taken in consideration, but it simply expresses a relation between orthobaric densities, and agrees excellently with experimental data as is shown in the following tables.

The calculation has been undertaken for the following 21 substances, which are possibly different in chemical nature : hydrogen, oxygen, nitrogen, argon, carbon dioxide, i-pentane, n-octane, benzene, hexamethylene, chlorobenzene, carbon tetrachloride, stannic chloride, methyl acetate, ethyl formate, propyl formate, methyl butylate, ethyl ether, methyl alcohol, ethyl alcohol,

(1) *Z. phys. Chem.*, **47** (1904), 471; **49** (1905), 129; **50** (1905), 238.

(2) *Proc. Nat. Acad. Sci.*, **3** (1917), 323.
J. Am. Soc. Refrig. Eng., **1** (1914), 9; **7** (1921), 371.
J. Am. Chem. Soc., **41** (1919), 589; **42** (1920), 54; **43** (1921), 1452.
J. Math. Phys. Mass. Inst. Tech., **1** (1922), 89, 191, 211 & 243.

(3) *Ann. Phys.*, **25** (1908), 569.

propyl alcohol and acetic acid. In this paper, however, abridged data[1] for only 8 substances are shown to save the space. Also the value expressed by the equation $q=RT \ln V+A/(V-E)$, has been calculated for liquid and vapour respectively, and they are given in the table as q_l and q_g. In the calculation the value of R is taken as 1.988 calories.

TABLE 1. Hydrogen.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
− 258.27°	0.07631	0.00020	175.1	178.0	278.3	275.4
− 253.76	0.07192	0.00101	163.9	164.3	294.4	294.0
− 247.79	0.06116	0.00405	138.6	137.6	319.2	320.2
− 245.73	0.06050	0.00613	124.2	124.1	327.4	327.5
− 240.57	0.04316	0.01922	52.2	54.0	341.5	339.7
	A=3958			E=4.20.		

(H. K. Onnes, Crommelin and Cath, *Verhl. Akad. Wet. Amst.*, **26** (1917), 192.)
(Mathias, Crommelin and Onnes, *Compt. rend.*, **172** (1921), 262.)

TABLE 2. Oxygen.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
− 210.4°	1.2746	0.0001	1.2×10^3	1175	1577	1.6×10^3
− 182.0	1.1415	0.0051	979	988	1594	1585
− 154.5	0.9758	0.0385	761	763	1606	1604
− 129.9	0.7781	0.1320	504	499	1634	1639
− 120.4	0.6032	0.2701	243	251	1622	1614
	A=18160			E=9.68		

(Mathias and Onnes, *Comm. Phys. Lab. Leiden*, No. 117 (1917).)

TABLE 3. Isopentane.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
0°	0.6393	0.0011	3459	3457	6026	(6028)
40	0.5988	0.004456	3051	3054	6047	6044
70	0.5656	0.01013	2742	2742	6075	6075
100	0.5278	0.02020	2420	2431	6133	6122
130	0.4826	0.03831	2032	2026	6146	6152
160	0.4206	0.07289	1511	1515	6161	6157
180	0.3498	0.1258	923	946	6138	6115
187.4	0.2761	0.1951	319	337	6079	6031
	A=204300			E=53.8.		

(Young, *Sci. Proc. Roy. Dublin Soc.*, **12** (1910), 374)

(1) Full data will be published in the *Journal of the Chemical Society of Japan.*

TABLE 4. Chlorobenzene.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
80°	1.0419	0.0008	5035	5062	8349	8322
100	1.0193	0.0014	4886	4863	8354	8377
120	0.9960	0.0026	4650	4657	8357	8350
140	0.9723	0.004316	4449	4452	8363	8360
160	0.9480	0.006784	4253	4254	8384	8383
180	0.9224	0.01023	4054	4054	8407	8407
200	0.8955	0.01506	3841	3841	8425	8425
220	0.8672	0.02145	3625	3623	8450	8452
240	0.8356	0.03000	3393	3385	8464	8472
260	0.8016	0.04172	3132	3131	8483	8484
		$A=292700$		$E=50.15$		

(Young, ibid.)

TABLE 5. Carbon tetrachloride.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
30°	1.5748	0.0012	4326	4339	7101	7088
60	1.5165	0.0033	4059	4054	7116	7121
90	1.4554	0.007955	3760	3762	7138	7136
120	1.3902	0.01639	3471	3470	7172	7173
150	1.3215	0.03040	3172	3173	7221	7220
180	1.2470	0.05249	2855	2851	7271	7265
210	1.1566	0.08787	2475	2479	7313	7309
240	1.0444	0.1464	2004	2023	7342	7323
270	0.8666	0.2710	1256	1326	7327	7257
		$A=232000$		$E=44.3$		

(Young, ibid.)

TABLE 6. Methyl acetate.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
0°	0.95932	0.0003	4400	4405	6765	(6760)
50	0.8939	0.002212	3855	3847	6688	6696
110	0.8060	0.01239	3181	3178	6651	6654
170	0.6907	0.04598	2388	2393	6621	6616
230	0.5427	0.2028	803	850	6479	6432
		$A=173700$		$E=37.8$		

(Young, ibid.)

TABLE 7. Ethyl ether.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
−101.3°	0.8435	0.40×10^{-6} (M.)	4976	4999	6526	6503
− 81.0	0.8227	3.61×10^{-6} (M.)	4711	4713	6433	6431
− 64.4	0.8056	15.74×10^{-6} (D.)	4499	4498	6374	6375
− 35.0	0.7749	12.59×10^{-5} (T.)	4129	4132	6291	6288
+ 20	0.7135	18.70×10^{-4} (Y.)	3467	3488	6197	6176
+ 60	0.6658	67.71×10^{-4} (Y.)	3039	3042	6179	6176
+ 90	0.6250	0.01477 (Y.)	2698	2699	6188	6187
+140	0.5385	0.04488 (Y.)	2040	2022	6181	6199
+190	0.3663	0.1620 (Y.)	749	769	6114	6094
		$A=185600$		$E=50.0$		

T : Taylor and Smith, *J. Am. Chem. Soc.*, **44** (1922), 2450.
D : Drucker and Kangro, *Z. physik. Chem.*, **90** (1915), 518.
M : Mündel, *Z. physik. Chem.*, **85** (1913), 456.
Y : Young, ibid.

Vapour densities with indices T, D and M have been calculated from vapour tensions given by these authors applying the ideal gas low, and those of liquid at low temperatures have been obtained by interpolation from above mentioned Taylor and Smith's results.

TABLE 8. Methyl alcohol.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
0°	0.8100	0.0000562	5195	5217	7214	7192
40	0.7740	0.0004394	4650	4652	6970	6968
80	0.7355	0.002084	4117	4120	6775	6772
120	0.6900	0.007142	3569	3569	6586	6586
160	0.6340	0.01994	2978	2973	6400	6405
200	0.5530	0.05075	2247	2225	6171	6193
230	0.4410	0.1187	1312	1315	5923	5920
237	0.3850	0.1607	886	890	5825	5821
239	0.3504	0.1878	645	638	5774	5771
		$A=78950$		$E=24.40$.		

(Young, ibid.)

These tables show that the deviation between two quantities $RT\ln V_g/V_l$ and $A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$ is in most cases less than one percent and it may be concluded that the equation (2) can be applied for whole range of orthobaric state without any considerable error. This relation holds even for

alcohols, which contain obviously associated molecules. Only for water it does not hold, because of the abnormal behaviour of its liquid phase.

Values of E used in the foregoing tables are approximately proportional to the critical volume V_k for normal liquids, as shown in Table 9. Consequently E should be an additive quantity, but the data are not sufficient to calculate out reliable additive constants for each atom or radical.

TABLE 9.

Substance	E	$V_{P=\infty}$	E/V_k	A	$T_k/\sqrt{AP_k}$
Hydrogen	4.20	—	0.0596	3958	0.148
Oxygen	9.68	—	0.130	18160	0.162
Nitrogen	12.8	—	0.142	17520	0.164
Argon	10.3	—	0.137	17440	0.165
Carbon dioxide	22.8	—	0.240	33600	0.195
Isopentane	53.8	—	0.175	204300	0.174
Normal octane	87.0	—	0.177	355900	0.180
Benzene	41.5	—	0.162	218500	0.174
Hexamethylene	52.6	—	0.171	249700	0.175
Chlorobenzene	50.15	—	0.163	292700	0.175
Carbon tetrachloride	44.3	—	0.161	232000	0.172
Stannic chloride	58.43	—	0.166	307600	0.176
Methyl acetate	37.8	—	0.166	173700	0.178
Ethyl formate	37.8	—	0.165	174000	0.178
Propyl formate	46.5	—	0.163	232700	0.173
Methyl butylate	59.2	—	0.174	276700	0.179
Ethyl ether	50.0	51.4	0.174	185600	0.181
Methyl alcohol	24.4	23.1	0.207	78950	0.205
Ethyl alcohol	37.8	33.6	0.226	105900	0.200
Propyl alcohol	48.6	—	0.221	143500	0.197
Acetic acid.	30.0	—	0.175	151100	0.202

As shown in Table 9 the ratio E/V_k is 0.169 in the mean, or E is about $V_k/6$ for normal liquids. For carbon dioxide and other abnormal liquids like alcohols the ratio is considerably higher and amounts to 0.21—0.24. The volume correction b in van der Waals' equation being about $V_k/4$ when extrapolated to $T=0$, so it can be said that E is about $2/3 \cdot b$ for almost all normal liquids.

G. Tamman[1] has given the following isothermal equation for liquids under high pressure :

$$(V - V_{P=\infty})(K+P) = A_T K.$$

(1) *Ann. Phys.*, **37** (1912), 975.

In this equation $V_{P=\infty}$ and K are constants independent of temperature and pressure, while A_T is independent of pressure but varies with temperature. $V_{P=\infty}$ is the molecular volume of the liquid under infinitely large pressure, and is given in the third column in Table 9, which has been obtained by interpolation. As is seen in the table the value of E is nearly equal to $V_{P=\infty}$ of Tammann.

For constant A, there exists a relation that the ratio $T_k/\sqrt{AP_k}$ is roughly constant for normal liquids. For abnormal liquids this ratio is larger than that for normal one, but for alcohols it approaches to that of normal liquids, as the number of carbon atoms in the molecules increases.

We can thus formulate as follows:

$$E=0.17\ V_k \quad \cdots\cdots(5)$$

$$A=32.3\frac{T_k^2}{P_k} \quad \cdots\cdots(6)$$

Putting $T/T_k=\theta$ and $V/V_k=\varphi$, we obtain from equations (5), (6) and (2),

$$R\theta \ln \frac{\varphi_g}{\varphi_l}=32.3\frac{T_k}{P_kV_k}\left(\frac{1}{\varphi_l-0.17}-\frac{1}{\varphi_g-0.17}\right)=1.47\left(\frac{1}{\varphi_l-0.17}-\frac{1}{\varphi_g-0.17}\right).$$

This equation is of reduced form and is in accord with the theory of the corresponding state, as the ratio P_kV_k/T_k is almost universal for normal liquids.

By slightly modifying the equation (2) we obtain

$$q=RT\ln V_g+\frac{A}{V_g-E}=RT\ln V_l+\frac{A}{V_l-E} \quad \cdots\cdots(7)$$

each side having V_g or V_l only. By actual calculation, it was found that q is a linear function of temperature, thus

$$q=C+BT \quad \cdots\cdots(8)$$

B, the temperature coefficient of q, is very small for normal liquids, and has considerable negative values for abnormal liquids. This enables us to calculate every pair of orthobaric densities as two roots of the equation (8), provided the values of C and B are known.

Next, an equation for vapour pressure at low temperatures can be derived from equation (2). By neglecting $A/(V_g-E)$, and regarding the vapour as an ideal gas, we can transform the equation (2) as follows:

$$\ln P=\ln\frac{RT}{V_l}-\frac{1}{RT}\frac{A}{V_l-E} \quad \cdots\cdots(9)$$

where vapour pressure P is given by the molecular volume of the liquid. As an example of the verification of this equation, the data for ethyl ether are given in the following table.

TABLE 10.

Temp. C.	Vapour press. (obs.) mm.	Vapour press. (calc.) mm.	Observer
−101°.3	0.058	0.0535	Mündel
− 95.2	0.118	0.118	,,
− 88.1	0.270	0.276	,,
− 81.0	0.584	0.588	,,
− 75.8	0.953	1.18	Drucker and Kangro
− 64.4	2.77	2.81	,, ,,
− 57.3	5.12	5.18	,, ,,
− 44.2	14.17	13.6	,, ,,
− 35.0	26.95	25.4	Taylor and Smith
− 32.4	31.93	30.1	,, ,,
− 20	63	63.7	Ramsay and Young
− 10	111.8	110	,, ,,
0	184.9	181	,, ,,

The vapour pressure calculated by the equation (9) agrees well with the observed value even at the temperature more than 100 degrees below the room temperature.

Sammary.

1. There exists a relation

$$RT\ln\frac{V_g}{V_l}=A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$$

between orthobaric densities for normal and abnormal liquids.

2. By modifying the above equation, we obtain

$$RT\ln V_g+\frac{A}{V_g-E}=RT\ln V_l+\frac{A}{V_l-E},$$

each side being proved to be a linear function of temperature.

3. For constants A and E it was found that $A=32.3\ \frac{T_k^2}{P_k}$ and $E=0.17\ V_k$ for normal liquids. E is, therefore, an additive quantity if V_k is additive.

4. By dint of the relation for constants A and E mentioned above, we have a reduced equation

$$R\theta\ln\frac{\varphi_g}{\varphi_l}=1.47\left(\frac{1}{\varphi_l-0.17}-\frac{1}{\varphi_g-0.17}\right).$$

5. For lower temperatures, we have derived a vapour pressure equation

$$\ln P = \ln\frac{RT}{V_t} - \frac{1}{RT}\,\frac{A}{V_t - E}.$$

The author wishes to express his sincere thanks to Prof. M. Katayama for his kind guidance throughout the present research.

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ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. III. THE ACTION ON PRIMARY ALIPHATIC ALCOHOLS.

By Harushige INOUE.

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Sabatier[1] and his co-workers have already described the dehydration of some primary alcohols by the catalytic action of alumina and other metallic oxides, and the experiments were reported by Ipatiew,[2] especially with regard to the formation of ethers and hydrocarbons of the olefine series from alcohols in presence of alumina, at different temperatures. The present experiment, therefore, was attempted by the writer to find some relation in the catalytic behavior on some aliphatic alcohols, between Japanese acid earth and alumina.

1. **Methyl Alcohol.** Forty gr. of methyl alcohol purified with lime, b.p. 65–66°, was passed on Japanese acid earth heated at 150°, 200°, 250°, 300°, 350° and 500° respectively at a rate of 14.4 c.c. per hour with a current of air or carbon dioxide gas. Of the reaction products, the qualitative and quantitative determinations of the gaseous substances were made by absorbing with bromine water, and also by the combustion method as usual, and of the liquid one by physical and chemical properties after fractional distillation. The results are shown in the following table.

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(1) Sabatier and Mailhe, *Bull. Soc. Chim.*, (4), 1 (1907), 137, 341, 524 & 773.
(2) Ipatiew, *Ber.*, 36 (1903), 1993.

TABLE 1.

Temp.	Gas	Alcohol & water		Gaseous subst.		Para-form-aldehyde
		gr.	d_{20}^{20}	C_2H_4 (%)	CO (%)	
150°	Air	20	0.8592	0.71	4.86	
	CO_2	30	0.8250	1.29	9.77	
200°	Air	13	0.9603			
250°	Air	13	0.9520	1.09	5.83	
	CO_2	25	0.8512	0.33	0.91	
300°	Air	17	0.9535	6.96	7.41	Trace
350°	Air	21	0.9772	28.05	4.03	0.03 (m.p. 157°)
	CO_2	27	0.9601	12.55	0.36	—
500°	Air	23	0.9905	26.73	5.20	0.06

The occurrence of formaldehyde and of its polymer para-aldehyde in the reaction product was confirmed by the characteristic odour and by the physical properties (m.p. 157–160°). The formation of ethylene, as is seen in the table, is favorable with high temperature, and the yield of carbon monoxide is greater in presence of air than in carbon dioxide.

The same experiment which was undertaken on methyl alcohol, has been extended to ethyl alcohol, isobutyl (b.p. 108°; $d_{15}^{15}=0.8075$) and isoamyl alcohol (b.p. 130–132°; $d_{15}^{15}=0.8189$; $[\alpha]^{18}=2°19'$), and the latter one, as will be seen from its physical constants, contains some active amyl alcohol as an impurity.

2. Ethyl Alcohol. Ethyl alcohol purified with silver oxide,[1] was examined by the same was as the case of methyl alcohol.

TABLE 2.

Alcohol gr.	Temp.	Vel. of alcohol c.c./h.	Alcohol & water gr.	Ether %	Ester %	Aldehyde %	C_2H_4 %
40	150°	21.26	25.27	5.73	14.73	about 1	1.72
„	200°	21.26	—	12.31	—	29.27	38.50
„	200°	51.87	11.40	53.02	—	2-3	15.30
„	250°	53.40	—	21.36	—	—	51.61
„	350°	17.83	—	—	—	—	95.71

The yield of ethylene from the alcohol, depends not only upon the rate of passing on catalyst, but on the reaction temperature. The formation of ether, which is due to the dehydration of alcohol as in the case of ethylene-formation, shows a maximum in yield at 200°. The oxidation of alcohol to aldehyde, the polymerisation of the oxidized substance into para-aldehyde (b.p. 120–124°) and the formation of ethyl acetate due to the dismutation of the aldehyde, were confirmed to occur simultaneously by the isolation of these reaction products in a fairly pure state.

(1) Dulap, *J. Am. Chem. Soc.*, **28** (1906), 395.

3. Isobutyl Alcohol. In the case of isobutyl alcohol, isobutylene and β-butylene are the main reaction products as mentioned by Ipatiew[1] and Senderens[2] in the catalytic action of alumina on the alcohol, and dibutyl ether (b.p. 140.9°; $d_{15}^{15}=0.7685$) and di-isobutylene (b.p.=110–113°; $d_{15}^{15}=0.7347$) were confirmed to occur in the reaction product by determining the physical constants of the corresponding fractions mentioned in the following table.

TABLE 3.

Temp.	Vel. of alcohol c.c./h.	Butylenes %	Liquid reaction products.	
			ice cooled gr.	water cooled gr.
150°	15	19.58	0.027 (0.11%)	4.807
250°	,,	57.25	0.229 (0.97%)	1.934
350°	,,	64.96		1.196

Temp.	Fraction	Yield gr.	d_{20}^{20}	n_D^{20}	Remark
150°	to 82°	2.9	0.7472	1.39619	
	103–105°	1.1	0.7840	1.39221	
	105–107°	0.7	0.7852	1.39932	
	107–140°	0.5	0.7794	1.40108	
	140–145°	0.3	0.7639	1.42310	Mostly di-butyl ether
	145–150°	0.9	0.7674	1.43287	
	above 200°	1.2	0.7829	1.43783	
250°	60–62°	1 drop			
	62–85°	—			
	85–110°	6 drops			
	110-113.5°	0.7	0.7344	1.41500	Di-isobutylene
	114–181°	0.6	0.7994	1.45287	
	Residue	0.3			
350°	to 90°	—			
	90–110°	0.2	0.7724	1.43887	
	Residue	0.5	0.8298	1.44326	

(1) Ipatiew, *Ber.*, **36** (1903), 1993.
(2) Senderens, *Bull. Soc. Chim.*, (4), **1** (1907), 692.

4. **Isoamyl Alcohol.** With amyl alcohol, as will be seen in Table 4, amylenes (isopropyl ethylene, methyl-ethyl-ethylene and trimethyl-ethylene), diamyl ether and diamylenes were confirmed to occur as usual in the lower fractions of the reaction product, and the yield of these substances tends to increase with the reaction temperature.

TABLE 4.

Temp.	Fraction	Yield gr.	d_{15}^{15}	n_D^{20}	Remark
150°	40–45°	0.7	0.6438(0°)	1.35836	Amylenes
	45–50°	0.9	—	1.35978	
	50–57°	1.1	0.7320(0°)		
	59–65°	1.1	0.7450(0°)		
	65–70°	1.4	0.7411(0°)	1.37639	
	70–75°	1.2	0.7444(0°)	1.37397	
	75–115°	0.2	0.7874(0°)		
	115–125°	0.3	0.8109(0°)		
	125–130°	10.8	0.8012	1.40867	Diamylenes & amyl alcohol
	130–135°	3.6	0.8027	1.40727	
	135–137°	5.7	0.7988	1.40925	
	170–175°	2.0	0.7783	1.41232	Diamyl ethers
	175–180°	1.3	0.7757	1.41331	
	180–185°	2.2	0.7875	1.41580	
	to 220°	2.2	0.7872	1.43341	
200°	28–33°	1.0		1.37252	Amylenes
	33–37°	2.0		1.37518	
	125–135°	1.4	0.7664	1.41820	Diamylenes & amyl alcohol
	150–160°	2.5	0.7743	1.42120	
	160–170°	0.5	0.7557	1.42440	Diamyl ethers
	170–177°	0.6	0.7693	1.45287	
	above 180°	2.9	0.8101		

TABLE 4. (Continued)

Temp.	Fraction	Yield gr.	d_{15}^{15}	n_D^{20}	Remark
250°	28–33°	2.0	0.6606	1.37667	Amylenes
	33–37°	3.4	0.6659	1.37931	
	37–90°	10 drops			
	90–100°	0.6	0.7658		
	120°(±1°)	0.4	0.7828		Diamylenes & amyl alcohol
	125–150°	0.7	0.7818		
	150–160°	1.2	0.7868	1.45797	
	160–200°	0.8	0.8168	1.48968	
	200–210°	0.6	0.8679	1.51153	
300°	28–33°	1.9	0.6646	1.37683	Amylenes
	33–37°	5.6	0.6672	1.37931	
	37–40°	1.2	0.6745	1.38186	
	40–110°	1 drop			
	110–120°	0.4	0.7618	1.42940	Diamylenes
	120–150°	3 drops			
	150–160°	1.1	0.8050	1.45507	
	Residue	1.3	0.8893	1.50831	
350°	28–33°	3.0	0.6590	1.37509	Amylenes
	33–37°	4.0	0.6700	1.37742	
	37–40°	1.3	0.6721	1.38243	
	40–110°	5 drops			
	110–120°	0.6	0.7848	1.44195	
	120–130°	4 drops			Diamylenes
	130–140°	1.1	0.8238	1.46949	
	140–142°	0.9	0.9010	1.49871	
500°	20–40°	1.0	0.5885		Amylenes
	40–140°	13 drops			
	140–144°	1.2	0.8720	1.49871	Diamylenes

By the contact action of Japanese acid earth, primary alcohols of the aliphatic series yield unsaturated hydrocarbons and ethers as in the case of the catalytic action of alumina, and also aldehydes and esters. Both the dehydration of alcohols and the polymerisation of unsaturated hydrocarbons and aldehydes, as we noticed in the present research, resulted in excellent yields at high temperature. The oxidation of alcohols and the dismutation of the oxidized substance, which occur with this catalyst but not with alumina, are favorable at low temperatures.

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SOME DERIVATIVES OF HYDROXYPHENYLGLYCINE.[1] I.

By **Kotaro SHIMO.**

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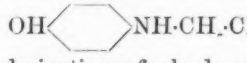
Alkyl and Aryl Derivatives of Hydroxyphenylglycine Nitrile.

1. p-Hydroxyanilidoacetonitrile (p-Hydroxyphenylglycine nitrile), 

Bucherer and Gtolée[2] synthesized some derivatives of p-hydroxyphenylglycine nitrile from potassium cyanide, p-aminophenol hydrochloride and acetone or benzaldehyde, and p-hydroxyphenylglycine nitrile has recently been synthesized by Galatis[3] by the condensation of p-aminophenol with formaldehyde and potassium cyanide in presence of sodium sulphite.

p-Hydroxyanilidoacetonitrile was obtained applying the principle used for the synthesis of anthranilidoacetonitrile by E. Kohner[4] from p-aminophenol, formaldehyde and potassium cyanide with 89–95% yield of the theory.

Twenty one gr. of finely powdered p-aminophenol was mixed with 50c.c. of glacial acetic acid to form a homogeneous paste, cooled with ice-water and then 20 gr. of finely powdered potassium cyanide and 20 c.c. of formaline

(1) This paper was read before the annual meeting of the Chemical Society of Japan, April 6th 1924 and at the monthly meeting, May 1st. 1926 and published in the *Osaka Kōgyōshiken-sho Hōkoku* (in Japanese), **5** (1924), No. 7, and will be published in the same publication, **7**, (1926).

(2) *Ber.*, **39** (1906), 986.

(3) *Helvetica Chim. Acta*, **4** (1921), 574.

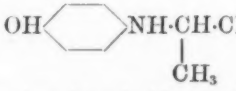
(4) *J. prakt. Chem.*, (2), **63** (1901), 392 ; also refer D.R.P. 117924; Friedländer, " Fortschritte der Teerfarben-fabrikation," VI (1900–1902), 572.

(Japanese Pharmacopœia) were added alternately in a portion of 2–3 gr. After all were added, the mixture was warmed at 70–80° for half an hour on a water bath and left to stand over night. On adding some water the nitrile was deposited, which was collected after cooling at 0°. The yield was 20 gr. The nitrile that remained in the mother liquor was extracted with ether, and after evaporating off the solvent there remained crystals weighing 5.5 gr. Total yield was 89% of the theory.

The condensation of p-aminophenol with formaline and potassium cyanide was carried out in aqueous solution ; 30 gr. of p-aminophenol hydrochloride was dissolved in 140 c.c. of water, and to a mixture of 17 c.c. of formaline (Japanese Pharmacopœia), 75 gr. of 20% aqueous potassium cyanide solution was added drop by drop with constant agitation and cooling it with ice-cold water during the reaction, thereby a voluminous greyish white precipitate was deposited. It was then warmed up to 60–70° and after all of the precipitate was dissolved the solution was cooled, and p-hydroxyphenylglycine nitrile was deposited as large transparent platy crystals. The yield was 29.1 gr. which corresponds to 95% of the theory. It melts at 103–104° (uncorr.) while Galatis described 100° as its melting point.

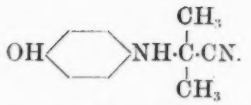
It gives a transient fuchsin-red coloration described by Galatis and also the same coloration with silver nitrate producing white precipitate, with ammoniacal silver nitrate a yellow color which changes to yellowish brown colloidal solution then greyish black precipitate, yellowish red coloration followed by effervescence with concentrated nitric acid, red coloration with Millon's reagent without warming, and orange coloration with potassium ferricyanide. On analysis, it gave the following results :

0.1619 gr. subst. gave 0.3859 gr. CO_2 and 0.0841 gr. H_2O. 0.0567 gr. subst. gave 8.85 c.c. N_2 (11.5°, 762 mm.). (Found : C=65.01 ; H=5.77 ; N=18.86. $C_8H_8ON_2$ requires C=64.87 ; H=5.41 ; N=18.92%).

2. **p-Hydroxyanilidomethylacetonitrile,** 

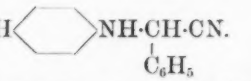
It was prepared from 10.8 gr. of p-aminophenol, 10 gr. of potassium cyanide, and 10 c.c. of 50% acetaldehyde in a manner described for the preparation of p-hydroxyanilidoacetonitrile. The yield of the crude nitrile was 7.6 gr. It was recrystallised from ether-ligroin solution in fine white microscopic leaflets which melt at 111–112° (uncorr.).

0.1220 gr. subst. gave 0.2985 gr. CO_2 and 0.0687 gr. H_2O. 0.1025 gr. subst. gave 14.85 c.c. N_2 (10°, 759.3 mm.). (Found : C=66.73 ; H=6.23 ; N=17.54. $C_9H_{10}ON_2$ requires C=66.67 ; H=6.17 ; N=17.28%).

3. **p-Hydroxyanilidodimethylacetonitrile,** 

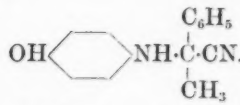
This substance was obtained from 5.4 gr. of p-aminophenol, 5 gr. of potassium cyanide and 5 c.c. of acetone in 12 c.c. of glacial acetic acid. The yield was 7.4 gr. The purified substance is fine snow-white leaflets and melts at 140–142° while Bucherer and others described 137° as its melting point.

0.1246 gr. subst. gave 0.3104 gr. CO_2 and 0.0764 gr. H_2O. 0.1044 gr. subst. gave 13.9 c.c. N_2 (10°, 763.7 mm.). (Found : C=67.94; H=6.81 ; N=16.25. $C_{12}H_{12}ON_2$ requires C=68.18 ; H=6.82 ; N=15.91%).

4. **p-Hydroxyanilidophenylacetonitrile,** 

From 5.4 gr. of p-aminophenol, 3.5 gr. of potassium cyanide dissolving in 20 c.c. of water and 5 gr. of benzaldehyde in 50% acetic acid solution, 9.5 gr. of crude nitrile was prepared which recrystallized from luke warm benzene. The pure nitrile was yellow colored small needle-shaped crystals melting at 122–124° (uncorr.), while Bucherer and others described 113–114° as its melting point.

0.1034 gr. subst. gave 0.2839 gr. CO_2 and 0.0512 gr. H_2O. 0.1498 gr. subst. gave 16.0 c.c. N_2 (12.5°, 761 mm.). (Found : C=74.88 ; H=5.50 ; N=12.85. $C_{14}H_{12}ON_2$ requires C=75.00 ; H=5.36 ; N=12.50%).

5. **p-Hydroxyanilidophenylmethylacetonitrile,** 

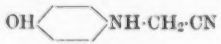
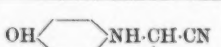
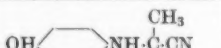
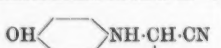
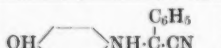
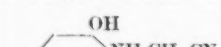
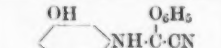
Twelve c.c. of glacial acetic acid, 5.4 gr. of p-aminophenol, 5 gr. of potassium cyanide and 10 gr. of acetophenone were treated in a similar manner as described in previous cases and 11.4 gr. of crude nitrile was obtained. It was purified from dilute alcoholic solution and melts at 128–130° (uncorr.).

0.1196 gr. subst. gave 0.3306 gr. CO_2 and 0.0674 gr. H_2O. 0.1044 gr. subst. gave 10.5 c.c. N_2 (11.5°, 757.7 mm.). (Found : C=75.39 ; H=6.26 ; N=12.08. $C_{15}H_{14}ON_2$ requires C=75.62 ; H=5.88 ; N=11.76%).

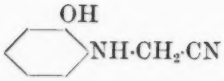
Alkyl or aryl derivatives of p-hydroxyanilidoacetonitrile described above, are soluble in both acid and alkali solutions (but aryl derivatives are insoluble in acid) and also in acetone, alcohol, ether, acetic ester, glacial acetic acid, chloroform and benzene, as I noticed in the case of p-hydroxyanilidoacetonitrile.

Other chemical behaviors of these substances towards ferric chloride, silver nitrate, Millon's reagent etc. are like those of the mother substance as will be seen in Table 1.

TABLE 1.

Substance.	Ferric chloride.	Silver nitrate.	Ammoniacal silver nitrate.	Conc. nitric acid.	Millon's reagent.	Potassium ferricyanide.
 m.p. 103–104°	fuchsin-red.	fuchsin-red producing white ppt.	yellow color → yellowish brown colloidal → greyish black ppt.	yellowish red.	red.	orange.
 m.p. 111–112°	brownish red.	pink → reddish violet producing white ppt.	brownish yellow colloidal → greyish ppt.	red.	yellow.	
 m.p. 140–142°	violet → chocolate color.	cobalt blue producing white ppt.	pale brownish grey colloidal → brownish grey ppt.	yellowish red.	yellow.	reddish brown.
 m.p. 122–124°	yellow.	yellow → brownish yellow ppt.	reddish orange colloidal.	reddish yellow.	yellow → colorless → brownish red.	
 m.p. 123–130°	bluish violet.	bluish violet producing white ppt.	greyish colloidal → brown → chocolate color.	yellowish red.	reddish orange.	
 m.p. 74–75°	yellowish red.	pale dirty red producing silver mirror accompanied with dirty brown ppt.	yellow → yellowish green → greyish black ppt.	red.	yellowish red.	reddish orange.
 m.p. 135–137°	brownish yellow.			yellowish brown.	red.	

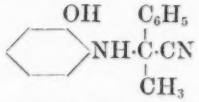
6. o-Hydroxyanilidoacetonitrile (o-Hydroxyphenylglycine nitrile),



o-Aminophenol reacts, in the same manner as p-isomer, in presence of glacial acetic acid with formaline and potassium cyanide producing o-hydroxyanilidoacetonitrile. 14.5 Gr. of the crude nitrile was actually obtained from 14.7 gr. of aminophenol. For the purification of the nitrile, the crude product was dissolved in ether, and to the ethereal solution ligroin was added until permanent turbidity began to occur, and the solution was left to evaporate slowly in vacuo or recrystallised from luke warm benzene. It melts at 74–75° (uncorr.), and is very easily soluble in ether, alcohol, acetone, acetic ester and glacial acetic acid, less so in chloroform, benzene and water but insoluble in ligroin. It is more easily saponifiable than the corresponding para compound ; when treated with warm water or dilute caustic alkalies, the evolution of ammonia is recognized. The color reactions of the nitrile are shown in Table 1.

0.1171 gr. subst. gave 0.2781 gr. CO_2 and 0.0608 gr. H_2O. 0.1058 gr. subst. gave 16.6 c.c. N_2 (8°, 766.4 mm.). (Found : C=64.77 ; H=5.81 ; N=19.29. C_8H_8ON requires C=64.87 ; H=5.41 ; N=18.92%).

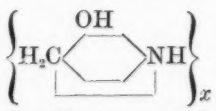
7. m-Hydroxyanilidophenylmethylacetonitrile,



This substance was obtained from 5.4 gr. of m-aminophenol, 12 c.c. of glacial acetic acid, 5 gr. of potassium cyanide and 9 c.c. of acetophenone in the manner described for the preparation of other nitriles. The yield was 5 gr. It was purified from ether-ligroin solution in fine white crystalline powder which melts at 135–137° (uncorr.). It is easily soluble in ether, alcohol, acetic ester and acetone, soluble in glacial acetic acid, less soluble in benzene and chloroform but insoluble in ligroin and water. The colour reactions of the nitrile are mentioned in Table 1.

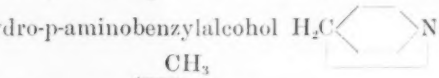
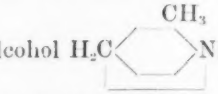
0.1093 gr. subst. gave 0.3047 gr. CO_2 and 0.0602 gr. H_2O. 0.1041 gr. subst. gave 10.2 c.c. N_2 (7.5°, 767.6 mm.). (Found : C=75.61 ; H=6.04 ; N=12.02. $C_{15}H_{14}ON_2$ requires C=75.62 ; H=5.88 ; N=11.76%).

8. Anhydro-p-amino-o-hydroxybenzylalcohol,



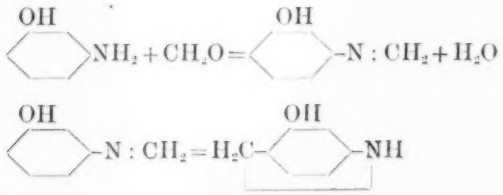
When 5.4 gr. of m-aminophenol was treated with 5 c.c. of formaline (Japanese Pharmacopœia) and 25 c.c. of 14% potassium cyanide solution in the manner described for the preparation of p-hydroxyanilidoacetonitrile, 6.3 gr. of a pale yellow amorphous powder was deposited which, after investiga-

tion of its insoluble nature in organic solvents and hydrochloric acid and melting point (does not melt under 300°), was regarded to be anhydro-p-amino-o-hydroxybenzylalcohol.

Moreover, the analytical results of the dried substance, and also the fact that anhydro-p-aminobenzylalcohol  and anhydro-p-amino-m-toluylalcohol  were synthesized from aniline and formaline, and o-toluidine and formaline, respectively,[1] give cause to presume it to be anhydro-p-amino-o-hydroxybenzylalcohol.

0.1340 gr. subst. gave 0.3430 gr. CO_2 and 0.0747 gr. H_2O 0.1159 gr. subst. gave 11.25 c.c. N_2 (8.5°, 761 mm.). (Found : C=69.28 ; H=6.19 ; N = 11.84. C_7H_7ON requires C=69.39 ; H=5.82 ; N=11.57%).

As to the formation of this substance, methylene-p-aminophenol would be formed as an intermediate reaction product from m-aminophenol and formaline, which soon converts to anhydrobenzylalcohol derivatives by the intermolecular rearrangement, before hydrocyanic acid enters into the condensation with the former hypothetical compound, as may be represented by the following scheme :



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(1) D.R.P., 95184; Friedländer, "Fortschritte der Teerfarben-fabrikation," IV (1894-1897), 52; *Ber.*, 33 (1900), 252.